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PHOTOCHEMICAL REDUCTION OF ZN-ETIOPORPHYRIN IN FROZEN SOLUTIONS: STRUCTURE OF REDUCED FORMS

[Fotokhimicheskoye vosstanovleniye Zn-etioporfirina v zamorozhennykh rastvorakh. Struktura vosstanovlennykh form.]

by

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It has been found that solutions of Zn-etioporphyrin in N-containing organic bases (lutidine, N-methylpiperidine, triethylamine), frozen at -196°, are capable of photochemical conversions. Comparison of the properties and spectral characteristics of the photoproducts formed with properties of protonated Zn-etioporphyrin dianions, produced by chemical methods, permits the following scheme to be proposed for conversion of Zn-etioporphyrin in organic bases (P, Zn-etioporphyrin molecule; D, molecule of base, which is both an electron donor and a proton donor to the P molecule). The first stage observable spectrally is photoreduction in the frozen solution: $P \xrightarrow{h\nu, D, -196°} PH^-$. Upon heating, the photoproduct incorporates a proton: $PH^- \xrightarrow{+H^+, D} PH_2$. The hydroderivative formed in frozen solution is capable of again splitting off a proton during irradiation: $PH_2 \xrightarrow{h\nu, -196°} PH^-$. Thermal addition of a proton to the PH^- and its subsequent photocleavage in frozen solution can be reproduced repeatedly in one and the same sample. The central metal atom has a significant effect on the photochemical behavior of a methyl-porphyrin in solution.

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(11)

Despite the successes achieved in investigation of metal-porphyrins in recent years [1,2], much remains unclear in the reaction mechamism of their photoreduction and the structure of the photoproducts formed. In spectral investigation of photo-conversion of Zn-EP[1] solutions in organic bases, frozen at -196°, we found that photochemical reduction of Zn-EP is possible under these drastic conditions, leading to formation of a hydro-derivative of the pigment. The spectral characteristics of this hydroderivative and, consequently, its structure, change upon heating and, upon subsequent cooling, can again be restored to the initial condition. The nature of these photochemical and thermal conversions of reduced forms of ZN-FP permits definite judgments to be expressed on their molecular structure.

Method: Photoreduction of Zr-EP in Frozen Solutions

We investigated photoconversion of Zn-EP and certain other M-EP in N-containing organic bases, frozen at -196° in triethylamine, in N-methylpiperidine, in 2,4-lutidine and in 2,4,6-trimethyl-piperidine. These compounds form a glass-like mass upon freezing, which provides conditions for conduct of spectral measurements. Of the compounds enumerated, the most transparent specimens at -196°are given by triethylamine and N-methylpiperidine. A thick network of cracks forms at this temperature in the 2,4-lutidine. A mixture of lutidine with triethylamine (~1:1) gives somewhat better results. The tests were carried out in flat glass vacuum

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[1]Abbreviations used in this article: M-EP is the metal derivative of etioporphyrin 1 (M is a metal atom).

cuvettes,3mm thick. The solutions were degassed before the start of the test. The concetration of M-EP was 5×10^{-5}-5×10^{-6} M. Irradiation was carried out with a DKSSh-1000 lamp with condenser, through various filters. The spectra were measured in a Shimazu Company SV-50A spectrophotometer.

The most complete photoconversion of Zn-FP took place in the triethylamine-lutidine mixture. After 30 min of irradiation by light in the 340-1000 nm region, the absorption bands of the initial pigment practically completely disappeared, and new ones appeared in place of them: at 450, 775 and 870 nm (see Figure, curves 1,2). In shorter exposures (1,5 and 10 min), intermediate stages of photoconversion of the pigment could be observed, in the course of which no other absorption bands at all, except the gradually decreasing bands of the initial Zn-EP enumerated, were found.

Upon heating the irradiated sample, at the time of its melting (about -90°), the 870 nm absorption band disappears and the bands of the initial Zn-EP increase. The 775 nm band disappears at -50° and the 450 nm band shifts to 457 nm (see Fig., curves 2,3). Further heating to +20° does not change the spectrum. The 457 nm band disappears upon admission of air and the initial Zn-EP band increases almost to the initial intensity.

It is evident that irradiation leads to the appearance of certain photoproducts, the stability of which is connected in diverse ways with temperature. Not having sufficient data on the nature of the photoproduct with the 870 nm band, we only discuss here the product with bands at 450 and 775 nm (the synchronism of

change in these bands and absorption leave no doubt that they belong to one product), as well as the product with a band at 457 nm. Protonated Zn-EP dianions, obtained by the action of a compound, a proton donor to the pigment dianions, in a mixture of tetrahydrofuran with diethyl ether, have spectra with the same absorption bands [3]. Such a full spectral congruence, together with the congruence of the chemical properties of the comparable products (the capacity of these products to be oxidized by oxygen to the initial pigment), are practically an adequate basis for asserting that irradiation of Zn-EP in a frozen mixture of triethylamine and lutidine leads to formation of protonated dianions, Zn-EP hydroderivatives. We turn to discussion of the structure and certain properties of the Zn-EP hydroderivatives in the following section of the article.

Irradiation of Zn-EP in 2,4-lutidine at -196° (exposure 20 min, 340-1000nm region) leads to practically complete conversion of the pigment into new products, among which is a product with bands at 450 and 775 nm, which changes, upon heating to 20°, into a product with a band at 457 nm, the pigment hydroderivatives. However, the yield of these products in lutidine is an order of magnitude less than in a mixture of lutidine with triethylamine. But then, the 870 nm absorption band has considerably greater intensity in lutidine, and strong absorption is observed in a decrease in the Soret band in the 430-440 nm region.

A similar picture is observed in other solvents which we studied: in all cases, formation of protonated dianions, accompanied by formation of byproducts in various ratios, can be

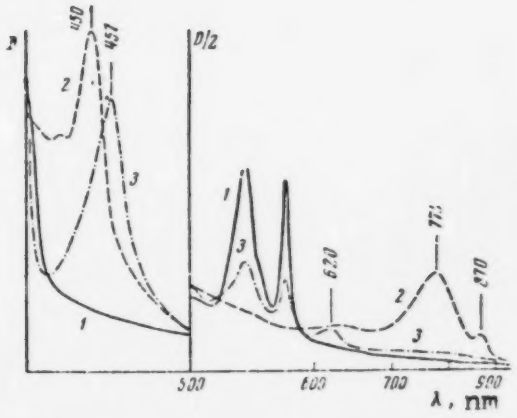
observed. The latter become unstable upon heating and are changed into the initial pigment.

Since, during the photoconversion of Zn-EP, intermediate stages in the pathway to formation of the hydroderivatives of this pigment were not found,there are no experimental data at all which could help to reveal details of the Zn-EP photoreduction reaction mechanism. Oxygen of the air does not affect photoconversion of Zn-EP in N-methylpiperidine.

Thermal and Photochemical Conversion of Hydroderivatives, Zn-EP: Structure of Reduced Forms

The phenomenon of thermal conversion of the photoproduct with bands at 450 and 775 nm into a product with a band at 457 nm was described in the preceeding section. It turned out that, by irradiation of a solution, frozen at -196° (the test was carried out in a mixture of lutidine with triethylamine), the product with a band at 457 nm can again be converted into a product with bands at 450 and 775 nm. The photoreaction takes place under light in the 370-500 nm region (or under the full light of the lamp), and is completed several times faster than the primary photoreaction of formation of the product with bands at 450 and 775 nm from the initial pigment. The alternating thermal and photochemical conversions of the protonated dianions can be repeated many times with one and the same sample.

In tests on protonation of Zn-EP dianions in a mixture of tetrahydrofuran with diethyl ether [3], the conclusion was drawn that the product with the absorption band at 485 nm is a dihydroderivative of the pigment PH_2 (the symbol P designates a molecule



Absorption Spectra of Zn-EP solution in mixture of triethylamine with lutidine at -196°: 1. before irradiation; 2. after 30 min irradiation; 3. after heating irradiated solution to 20° and cooling to -196°

of the initial Zn-EP). There were not sufficient data for an unambiguous conclusion as to the structure of the product with two bands, and it can be hypothesized that it is either a complex of the dihydroderivative with some molecule (ion) from the surrounding medium or the partially protonated dianion PH^-. Experiments on the photochemical and thermal conversions of Zn-EP in a mixture of triethylamine and lutidine, permits the second of these two possible structures to be preferred. In fact, it is difficult to imagine how a complex of the PH_2 molecule with a neighboring molecule can be formed in frozen solution, by irradiation of the PH_2 product (with one band at 457 nm). Evidently, the product with two bands (at 450 and 775 nm) should be assigned the structure PH^-. In this case, the photochemical and thermal conversions of Zn-EP, which we observed in the mixture of triethylamine and lutidine, can be represented by the following scheme.

Photochemical formation of PH^-:

$$P \xrightarrow{-196^\circ, D, h\nu} PH^- \text{ (product with bands at 450 and 775 nm)}$$

(here, D is a molecule of the base, which is an electron and proton donor with respect to molecule P). It is obvious that a number of intermediate stages precede formation of PH^-: the primary electron transfer act, proton transfer, addition of a second electron. For the present, nothing can be said of the sequence of these stages or of their mechanism.

Thermal conversion of PH^- to the dihydroderivative:

$$PH^- \xrightarrow{-196^\circ, D} PH_2 \text{ (product with band at 457 nm).}$$

Photochemical splitting of a proton from the dihydroderivative:

$$PH_2 \xrightarrow{-196^\circ, h\nu} PH^-$$

It can be thought that the proton freed in this conversion is bound to a molecule of the base, forming a DH^+ type cation. It should be noted that, in the presence of air, the reaction of photocleavage of the proton from PH_2 does not take place in the frozen solution. Apparently, oxygen deactivates the excited state of the PH_2 molecule, from which it splits a proton, with quite great speed. At 20°, in the presence of air, PH_2 is slowly oxidized to the initial P.

Dependence of Photoconversion of M-EP on Central M Atom

Mg-EP, in a mixture of triethylamine and lutidine, also undergoes photochemical and thermal conversions, like Zn-EP. Irradiation of the initial pigment at -196° leads to formation of the product PH^- with absorption bands at 453 and 780 nm. At 20°, this photoproduct is converted to PH_2, with an absorption

band at 463 nm. Ni-EP and Cu-EP have practically no photosensitivity under the same test conditions. Cu-EP in N-methylpiperidine behaves completely differently. In a frozen solution, formation of molecular complexes of Cu-EP with N-methylpiperidine takes place. Irradiation of the frozen solution leads to dissociation of the complex into the components and to formation of a reduced form of the pigment, with an unknown structure. A seperate article will be devoted to thorough analysis of this phenomenon. ClFeIII-EP (chlorferrietioporphyrin) in a mixture of triethylamine and lutidine, has an absorption spectrum which is significantly different from its spectrum in diethyl ether, which can be explained by formation of a pigment-base complex. The spectrum of the solution changes little upon cooling from 20 to -196°. Irradiation of the solution, frozen at -196°, with light in the 340-1000 nm region leads to conversion of the pigment into FeII-EP (ferroetioporphyrin), with its typical absorption spectrum [4], which does not change upon further irradiation. We note that photochemical reduction of chlorferrietioporphyrin to ferroetioporphyrin takes place with much greater speed in a liquid mixture of triethylamine and lutidine.

What is the reason for the sharp difference in photochemical properties of various M-EP? It can be hypothesized that the initial event of the photoreduction reaction, electron transfer from a molecule of the reducer to a M-EP molecule, is accomplished through the M atom. If the M in the molecule has insufficient electron affinity, the reduction reaction generally does not take

place (Ni-EP, FeII-EP). The FeIII atom, in the chlorferrietioporphyrin, apparently has the greatest electron affinity. However, in this case, the reaction is interrupted at the first stage, in the course of which the electron being added is localized on the Fe atom. To accomplish further conversions, the electron being added must be transferred from the M atom to the tetrapyrrole ligand of the pigment molecule. It is possible that just this process takes place in reduction of Zn-EP and Mg-EP. We have not considered the electron acceptor properties of the tetrapyrrole ligand in the optically excited state in these discussions. Undoubtedly, it also plays a definite part in the tetrapyrrole pigment photoreduction reactions (the possibility of photoreduction of non-metal pigments under similar conditions is evidence of this [1,2]). In addition to that, the photosensitivity of pigments in frozen solutions must inevitably depend on the configuration of the immediate surroundings of the M-EP molecule, in particular, on whether or not the M-EP forms complexes with surrounding molecules. At the present time, there are still no quantitative criteria for evalaation of the set of factors determining photosensitivity of M-EP in frozen solutions. Undoubtedly, however, the electron affinity of the central M atom in the pigment molecule plays a definite part in this respect.

* * *

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Bibliography

1. Sidorov, A. N., in the collection Elementarnyye fotoprotsessy v molekulakh [Elementary Photoprocesses in Molecules], Nauka Press, Moscow-Leningrad, 1966, p 267.

2. Sidorov, A. N., in the collection Molekulyarnaya fotonika [Molecular Photonics], Nauka Press, Leningrad, 1970, p 109.

3. Sinyakov, G. N., Gurinovich, G. P., Maslov, V. G. and Sidorov, A. N., Zh. prikl. spektrosk., 14, 1971, p 849.

4. Sidorov, A. N. and Yestigneyeva, R. P., Teor. Eksper. Khim., 3, 1967, p 647.